



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) Publication number : **0 552 983 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **93300487.1**

(51) Int. Cl.⁵ : **C09D 183/07, C08J 3/03,
B60R 21/16**

(22) Date of filing : **22.01.93**

(30) Priority : **23.01.92 JP 34201/92**

(43) Date of publication of application :
28.07.93 Bulletin 93/30

(84) Designated Contracting States :
DE FR GB

(71) Applicant : **SHIN-ETSU CHEMICAL CO., LTD.**
6-1, Ohtemachi 2-chome
Chiyoda-ku Tokyo (JP)

(72) Inventor : **Inoue, Yoshio**
No. 3-21, Isobe 4-chome
Annaka-shi, Gunma-ken (JP)
Inventor : **Morii, Kazuma**
No. 12-37, Isobe 3-chome
Annaka-shi, Gunma-ken (JP)

(74) Representative : **Stoner, Gerard Patrick et al**
Mewburn Ellis 2 Cursitor Street
London EC4A 1BQ (GB)

(54) **Coating compositions and air bags coated with them.**

(57) An air bag coating composition is obtained by emulsifying (A) an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom, (B) an organo-hydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon atom, and (C) a curing catalyst in water in the presence of an emulsifier to form an aqueous silicone emulsion. The composition cures into a coating which firmly adheres to an air bag base fabric and provides a tack-free surface.

EP 0 552 983 A2

BEST AVAILABLE COPY

This invention relates to an air bag coating composition suitable for air bags and, more preferably, to coating compositions suitable for forming a cured silicone coating which adheres firmly to an air bag base fabric and can provide a substantially tack-free surface. In another aspect it relates to air bags having a coating of such a composition cured onto a base fabric.

For safety, advanced automobiles are now fitted with air bags which are normally folded and received in the steering wheel, but upon detection of collision shocks, can be instantaneously inflated between the wheel and the driver to help protect the driver from injury. The air bags are generally formed from nylon fabric by coating it with chloroprene rubber. These air bags have a short life, since chloroprene rubber is poorly resistant to heating and weathering. The air bags are also required to be flame retardant so that they are resistant against any fire or explosion which may break out upon collision of the car. Since chloroprene rubber is not very flame retardant, prior art air bags formed from chloroprene rubber-coated fabric are further coated with a flame retardant silicone at locations where they might be exposed to a blast.

Air bags formed from silicone rubber-coated fabric have the advantage of eliminating need for a flame retardant coating, because well-known flame retardants can be blended in the silicone rubber to render the rubber itself flame retardant. Air bag manufacturers are becoming more interested in silicone rubber coating compositions, for that reason and because of their heat resistance and weather resistance.

A typical air bag using silicone rubber-coated fabric has a design whereby it is normally folded within the automotive steering wheel, but instantaneously inflated when explosive gas is injected upon collision. On inflation, the coating applied to the air bag fabric is instantaneously stretched along with the air bag fabric. Thus not only the base fabric but also the coating should be mechanically strong. To this end, the currently available silicone coating compositions use base polymers of relatively high molecular weight, as well as containing curing agents, flame retardants, adhesion aids, reinforcements and other additives.

The coating compositions using high molecular weight base polymers, however, are quite difficult to apply to the coating thickness of 40 to 100 μm normally required for air bags using knife coaters, offset roll coaters, gravure coaters or the like. The coating compositions must therefore be diluted with organic solvents to a viscosity low enough to allow easy coating onto the base fabric.

However, the use of organic solvents has serious problems including the risk of electrostatic ignition and potential hazard to operators' health since organic solvents can be taken into the body by way of inhalation or skin contact. Cured coatings are formed on base fabric by applying an organic solvent-diluted liquid of the coating composition and causing the solvent to evaporate off. The evaporated organic solvent must be recovered at any expense since otherwise it causes air pollution.

Among means for changing a coating composition to a solventless system, the simplest way is to reduce the degree of polymerization of the basic polymer until the viscosity of the composition is reduced to a sufficient level to allow for coating by means of a knife coater or the like. However, a coating composition based on a polymer having a lower degree of polymerization forms a cured coating which tends to be low in mechanical strength so that the coating can crack upon air bag inflation and allow hot explosive gas to bleed out.

If the viscosity of a coating composition is reduced too far, the composition will strike through base fabric, typically plain weave fabric of nylon fibers, resulting in a less smooth surface. If the composition on the fabric rear surface is cured as struck-through and then wound up, the coated fabric gives rise to blocking. Additionally, the struck-through composition will adhere to rolls of the coating machine, adversely affecting operating efficiency and outer appearance. It is thus desired to have a silicone rubber coating composition having an adequate viscosity to allow coating without the need for organic solvent for dilution.

Furthermore, conventional silicone rubber coating compositions tend to form cured coatings which are tacky on their surface, also contributing to a blocking problem.

The general problem addressed herein is to provide novel silicone-based compositions which are suitable for use in coating air bag fabric, as well as fabrics such as air bag fabrics coated therewith.

In particular, preferred aims include the provision of an air bag coating composition which (i) is free of organic solvent, (ii) cures to a coating having firm adhesion to an air bag base fabric, and (iii) has a tack-free surface. The achieving of a good working viscosity is a particularly preferred aim.

The present invention provides a coating composition in the form of an aqueous silicone emulsion comprising (A) an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom in a molecule and having a viscosity of at least 300 centistokes at 25°C, (B) an organohydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon atom in a molecule, and (C) a curing catalyst. Components (A), (B) and (C) are emulsified in water in the presence of an emulsifier to form the aqueous silicone emulsion. We find that such emulsions may be applied to air bag base fabric, such as plain weave fabrics of polyamide, polyester or the like and then cured, to obtain cured coatings which may have higher adhesion to the base fabric than coatings obtained by diluting the same components (A), (B) and (C) with an organic solvent. Also, we found that the cured coatings present a tack-free surface. In addition, they have good rubbery

properties so that they resist cracking upon air bag inflation.

The aqueous silicone emulsion has a suitable viscosity to apply to the base fabric without diluting with organic solvent. The eliminated use of organic solvent insures a good working environment. The emulsion produces no hazard to the operator's health. The emulsion readily cures at room temperature typically by simply removing water. It cures at a much higher rate if heated. In either case, it forms a cured coating having good rubbery properties including strength, elongation and hardness. Thus the aqueous silicone emulsion is a useful coating composition for air bags.

An air bag is also contemplated herein which includes a base fabric having applied thereon a cured coating of an above-defined composition.

A method of preparing an air bag is contemplated which comprises the steps of applying to an air bag fabric an air bag composition in the form of an aqueous silicone emulsion comprising (A) an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom in a molecule and having a viscosity of at least 300 centistokes at 25°C, (B) an organohydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon atom in a molecule, and (C) a curing catalyst, and curing the air bag composition to form a cured coating, preferably having firm adhesion to the air bag fabric and a substantially tack-free surface.

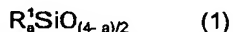
BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 schematically illustrates a surface tack test employed in the Example and Comparative Example.

FIG. 2 schematically illustrates a test for examining cured properties in the Example and Comparative Example.

DETAILED DESCRIPTION

Component (A) used herein is an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom in a molecule. The alkenyl groups include vinyl and allyl groups and mixtures thereof. No limits are imposed on organic groups other than the alkenyl groups attached to a silicon atom, molecular structure, degree of polymerization and the like. Preferably, component (A) is an organopolysiloxane of the following general formula:

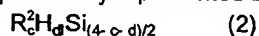


wherein R^1 , which may be identical or different, is a substituted or unsubstituted monovalent hydrocarbon group, preferably having 1 to 12 carbon atoms, especially 1 to 6 carbon atoms, and letter a is a positive number of 1.98 to 2.01. Examples of the monovalent hydrocarbon group include alkyl groups such as methyl, ethyl, propyl, butyl and hexyl groups; alkenyl groups such as vinyl and allyl groups; aryl groups such as phenyl and tolyl groups; and substituted ones of these groups wherein some or all of the hydrogen atoms are replaced by halogen atoms, cyano groups or the like, such as chloromethyl, 3,3,3-trifluoropropyl and cyanoethyl groups. Preferred groups represented by R^1 are methyl, ethyl, phenyl, γ -trifluoropropyl, cyanoethyl, vinyl and allyl groups. The organopolysiloxane in one preferred aspect contains two or more alkenyl groups as defined above and at the same time at least 50 mol%, especially at least 80 mol% of a methyl group. With a methyl content of less than 50 mol%, the properties inherent to methylpolysiloxane tend to be undesirably lost and the material cost would become higher.

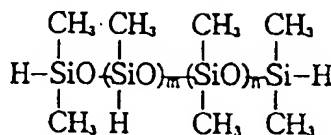
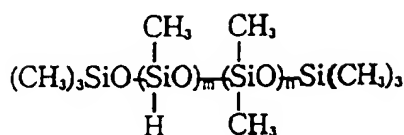
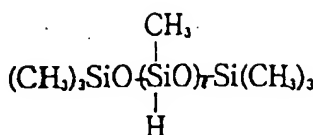
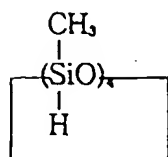
The organopolysiloxane should have a viscosity of at least 300 centistokes (cs) at 25°C, especially 1×10^4 to 1×10^8 cs at 25°C. With a viscosity of less than 300 cs, the coating composition tends to form a coating having mechanical strength below the practically acceptable level.

These organopolysiloxanes should preferably have a substantially linear molecular structure. The organopolysiloxanes are often blocked with a silanol, methyl or vinyl group, preferably with a trivinylsilyl group at the end of their molecular chain. The organopolysiloxanes may be prepared by conventional well-known methods, for example, by subjecting cyclic polysiloxanes which are well-known oligomers to ring-opening polymerization in the presence of acid or alkali.

Component (B) is an organohydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon atom ($\equiv SiH$) in a molecule. It preferably represented by the following general formula:



wherein R^2 is an alkyl group having 1 to 10 carbon atoms such as methyl, letters c and d are positive numbers with the sum of c and d being 1 to 3. Some illustrative, non-limiting examples of the organohydrogenpolysiloxane are represented by the following structural formulae.



15 In the formulae, ℓ , m and n are integers.

Component (B) is preferably blended in an amount to provide 0.5 to 4 $\equiv \text{SiH}$ bonds per alkenyl group of component (A) and at the same time, in an amount of about 0.5 to 30 parts by weight per 100 parts by weight of component (A) in order to provide improved adhesion of the coating composition to base fabric. If the amount of component (B) exceeds 30 parts on this basis, the resulting cured coating tends to remain somewhat tacky on the surface and be insufficiently strong to prevent cracking.

Component (C) is a curing catalyst which may be selected from conventional platinum series catalysts. It is effective for promoting addition reaction between the alkenyl group in the organopolysiloxane as component (A) and the $\equiv \text{SiH}$ bond in the organohydrogenpolysiloxane as component (B). Exemplary catalysts are platinum black, chloroplatinic acid, alcohol modified chloroplatinic acid, and complex salts of chloroplatinic acid with vinyl siloxanes. The catalyst is added in a catalytic amount, preferably in an amount of about 10 to 5,000 ppm, more preferably about 50 to 1,000 ppm based on the weight of component (A).

When platinum or platinum compounds as mentioned above are added to the composition, there is the risk that the composition undergoes scorching during storage. To prevent this undesirable phenomenon, a reaction retarder is preferably used in combination with the platinum catalyst. Exemplary retarders are methylvinylsiloxane, acetylene alcohol, and acetylene alcohol whose hydroxyl group is blocked with a trimethylsilyl group. The retarder, when used, is added in an amount of about 0.01 to 10 parts, preferably about 0.05 to 5 parts by weight per 100 parts by weight of component (A).

In order to enhance the adhesion of the coating composition to base fabric, any of well-known adhesive aids such as organo-functional silanes and amino-functional silanes may be added to the coating composition. Also reinforcements such as colloidal silica may be added for reinforcing purposes.

The coating composition is in the form of an aqueous silicone emulsion which is prepared by emulsifying a blend containing components (A) to (C) in water in the presence of an emulsifier.

Suitable emulsifiers for use herein include anionic and nonionic surfactants, for example, sulfonic acids, sulfuric acids, phosphoric acids and salts thereof capable of surface activation, more illustratively, alkylsulfates such as sodium laurylsulfate, aliphatic hydrocarbon group-substituted benzenesulfonates such as sodium dodecylbenzenesulfonate, aliphatic hydrocarbon group-substituted naphthalenesulfonates, polyethylene glycol sulfates, and lauryl phosphates.

Preferably the emulsifier is used in an amount of about 0.3 to 20 parts, more preferably about 0.5 to 5 parts by weight per 100 parts by weight of the organopolysiloxane as component (A). Less than 0.3 parts of the emulsifier on this basis would be less effective for helping emulsification, often failing to form an aqueous emulsion. More than 20 parts of the emulsifier would eventually yield an elastomer having low rubbery properties including strength, elongation and hardness.

Water is used in any desired amount to ensure formation of an aqueous emulsion suitable as an air bag coating composition. Often about 25 to 600 parts, especially about 50 to 200 parts by weight of water is used per 100 parts by weight of the organopolysiloxane as component (A).

The aqueous emulsion may be prepared by mixing components (A), (B) and (C) and thereafter mixing them with an emulsifier and water. Alternatively, components (A), (B) and (C) are respectively mixed with an emulsifier and water to form aqueous emulsions, which are then mixed together.

If it is desired to increase the viscosity of the coating composition at application, polyvinyl alcohol or similar thickeners may be added to the composition.

The base fabrics to which the coating composition is cured may be e.g. fibers of nylon, Tetron, Vinyon, polyester and polyurethane and woven fabrics thereof, with nylon and polyester being preferred. A plain weave is the most useful weave.

The coating composition may be applied to base fabric by any desired coating technique, for example, calendering, knife coating, brush coating, dipping, or spraying.

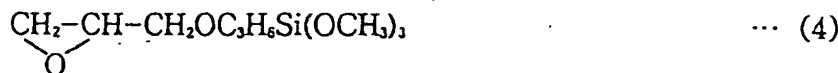
Thereafter, the coating is cured simply by allowing to stand at room temperature while removing water, but preferably by hot air vulcanization at 100 to 180°C for several seconds to about 20 minutes. Then cured products having a varying crosslinking density covering silicone rubber, silicone resin and silicone gel are obtained depending on the particular components used.

EXAMPLE

Examples are given below (by way of illustration and not by way of limitation). All parts are by weight.

Example and Comparative Example

A composition designated A was prepared by mixing 100 parts of a methylvinylsiloxane consisting of 99.85 mol% of dimethylsiloxane unit and 0.15 mol% of methylvinylsiloxane unit, end-blocked with a dimethylvinylsiloxy group and having an average degree of polymerization of about 8,000 with 1.3 parts of a methylhydrogenpolysiloxane of the following formula (3), 0.05 parts of ethyl cyclohexanol as an addition reaction controlling agent, 100 ppm of platinum, and 3 parts of epoxy carbon functional silane of the following compositional formula (4). The blend was then mixed with 100 parts of water and 10 parts of dodecylbenzenesulfonate by means of a combination mixer to form an aqueous silicone emulsion, and polyvinyl alcohol was added to the emulsion for adjustment to a viscosity of about 100 poise.



For comparison purposes, another composition designated B was prepared as above except that water, dodecylbenzenesulfonate and polyvinyl alcohol were omitted and instead, the blend was diluted with toluene to a viscosity of about 100 poise.

Each of the coating compositions A and B was applied to one surface of plain weave fabric of 420-denier nylon filaments (46 filaments/inch in warp and weft) to a dry coating thickness of about 100 μm . The coating was cured by allowing it to stand at a temperature of 25°C and a relative humidity of 60% for 48 hours. There was obtained a coated fabric.

These samples were examined by the tests shown in FIGS. 1 and 2 wherein the coated fabric is shown with a nylon fiber fabric 1 and a cured silicone coating 2.

For examining tackiness, a tensile test was carried out as shown in FIG. 1. Two pieces of the coated fabric were mated together such that the coatings 2 faced each other. They were compression bonded at 25°C under a pressure of 20 kgf/cm² for 12 hours and cut into a strip of 2.5 cm wide. Using a tensile tester, a 180° peel test was carried out as shown in FIG. 1. With one piece fixed, the free end of the other piece was pulled back at a rate of 10 mm/min. to measure the load required to peel the other piece from the one piece. The load indicates the surface tack of the cured silicone coatings.

Also, the samples were examined for cured property as shown in FIG. 2. The sample was scratched on the cured silicone coating 2 surface by moving back and forth a stainless steel tool 3 with a weight 4 of 200 grams resting thereon. The number of strokes of the scratching tool taken before the cured silicone coating 2 was torn off from the nylon fabric 1 indicates the adhesion of the silicone coating to the nylon fabric.

The results are shown in Table 1.

Table 1

	Example	Comparative Example
Composition	A	B
Type	aqueous emulsion	solvent type
Viscosity, poise	100	100
Tack, g/2.5 cm wide	0*	200
Adhesion, strokes	> 100	50

* separated by itself after compression bond

There has been described a coating composition adapted to apply to air bag base fabric which forms a cured coating having improved adhesion to the base fabric and a tack-free surface. The composition can be adjusted to an adequate viscosity to apply without the need for organic solvent. Due to the eliminated use of organic solvent, the composition is fully safe during application and not harmful at all to the operator.

Claims

1. An air bag coating composition in the form of an aqueous silicone emulsion comprising
 - (A) an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom in a molecule and having a viscosity of at least 300 centistokes at 25°C,
 - (B) an organohydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon atom in a molecule, and
 - (C) a curing catalyst.
2. A composition of claim 1 wherein components (A), (B) and (c) are emulsified in water in the presence of an emulsifier to form the aqueous silicone emulsion.
3. A composition of claim 1 or 2 wherein component (A) is an organopolysiloxane of the general formula:

$$R^1_n SiO_{(4-a)/2} \quad (1)$$
 wherein R¹ is independently a substituted or unsubstituted monovalent hydrocarbon group and letter a is a positive number of 1.98 to 2.01.
4. A composition of any preceding claim wherein component (B) is an organohydrogenpolysiloxane of the general formula:

$$R^2_c H_d Si_{(4-c-d)/2} \quad (2)$$
 wherein R² is an alkyl group, letters c and d are positive numbers with the sum of c and d being from 1 to 3.
5. A composition of claim 2 wherein said emulsifier is an anionic or nonionic surfactant.
6. A composition of any preceding claim which contains
 - 100 parts by weight of component (A),
 - 0.5 to 30 parts by weight of component (B), and
 - a catalytic amount of component (C).
7. A composition of claim 2 which contains
 - 100 parts by weight of component (A),

0.5 to 30 parts by weight of component (B),
 a catalytic amount of component (C),
 0.3 to 20 parts by weight of the emulsifier, and
 25 to 600 parts by weight of water.

- 5 8. An air bag comprising a base fabric having applied thereon a cured coating of the composition of any one of claims 1 to 7.
9. A method of preparing an air bag comprising the steps of
 10 applying to an air bag fabric an air bag composition in the form of an aqueous silicone emulsion comprising
 (A) an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom in a molecule and having a viscosity of at least 300 centistokes at 25°C,
 (B) an organohydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon
 15 atom in a molecule, and
 (C) a curing catalyst, and
 curing the air bag composition to form a cured coating adhering to the air bag fabric.

FIG.1

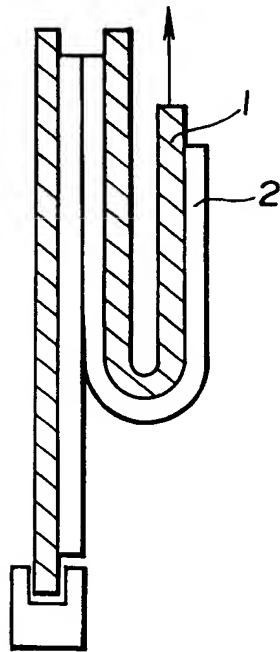
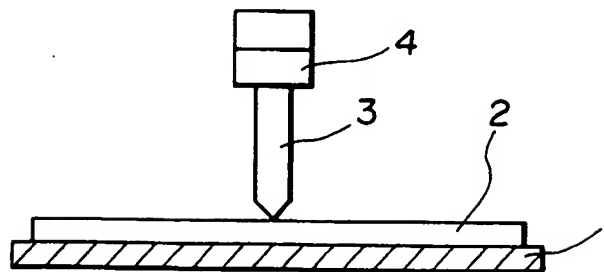


FIG.2





11 Publication number: **0 552 983 A3**

12

EUROPEAN PATENT APPLICATION

21 Application number: **93300487.1**

51 Int. Cl.⁵: **C09D 183/07, D06M 15/643,
C08J 3/03, B60R 21/16**

22 Date of filing: **22.01.93**

30 Priority: **23.01.92 JP 34201/92**

43 Date of publication of application:
28.07.93 Bulletin 93/30

84 Designated Contracting States:
DE FR GB

88 Date of deferred publication of search report:
13.10.93 Bulletin 93/41

71 Applicant: **SHIN-ETSU CHEMICAL CO., LTD.**
6-1, Ohtemachi 2-chome
Chiyoda-ku Tokyo (JP)

72 Inventor: **Inoue, Yoshio**
No. 3-21, Isobe 4-chome
Annaka-shi, Gunma-ken (JP)
Inventor: **Momii, Kazuma**
No. 12-37, Isobe 3-chome
Annaka-shi, Gunma-ken (JP)

74 Representative: **Stoner, Gerard Patrick et al**
Mewburn Ellis 2 Cursitor Street
London EC4A 1BQ (GB)

54 Coating compositions and air bags coated with them.

57 An air bag coating composition is obtained by emulsifying (A) an organopolysiloxane containing at least two alkenyl groups each attached to a silicon atom, (B) an organo-hydrogenpolysiloxane containing at least three hydrogen atoms each attached to a silicon atom, and (C) a curing catalyst in water in the presence of an emulsifier to form an aqueous silicone emulsion. The composition cures into a coating which firmly adheres to an air bag base fabric and provides a tack-free surface.

EP 0 552 983 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 0487

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	CHEMICAL ABSTRACTS, vol. 116, no. 12 Columbus, Ohio, US; abstract no. 108237k, * abstract * & JP-A-3 243 442 (TORAY INDUSTRIES) ---	1-9	C09D183/07 D06M15/643 C08J3/03 B60R21/16
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 158 (C-586)17 April 1989 & JP-A-63 314 275 (SHIN-ETSU) 22 December 1988 * abstract *	1-9	
P,Y	& US-A-5 095 067 (Y. HARA ET AL.) * column 1, lines 6-9; example 1; claims 1-3 *	1-9	
A	FR-A-2 401 195 (GENERAL ELECTRIC) * example; claim 1 *	1-9	
A	EP-A-0 084 772 (BAYER) * claims 1, 4 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C09D D06M
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 11 AUGUST 1993	Examiner HOEPFNER W.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>Δ : member of the same patent family, corresponding document</p>			

EPO FORM 1501 (03.92) (P0401)